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## (54) MANUFACTURE OF ELECTRODE FOR NONAQUEOUS ELECTRIC BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrode which has an improved charge/discharge characteristic and a physical characteristic of discharge capacity, a charge/ discharge cycle life, etc., by pulverizing flake graphite twice or more and mixing and pulverizing it using active material.

SOLUTION: Available positive electrode active material is a lithium containing metallic oxide, or a similar metallic sulfide, and negative electrode active material is preferably hard non-graphitized carbon or polymer carbon. When a flake graphite is pulverized to a desired grain size with a jet mill or the like, and is separated and pulverized in a ball mill or the like so as to be cleaved, its grain size hardly changes and its thickness becomes thin. With such twice or more of pulverizing graphite's grain size remains large and increases its specific surface area. By mixing and pulverizing the pulverized graphite and active material, contact surface with the active material is formed on the graphite such that its grain size is kept not to be small. When the central grain size of the graphite is larger than, preferably more than two times, the central grain size of the active material, more excellent effect is provided.

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

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**CLAIMS**

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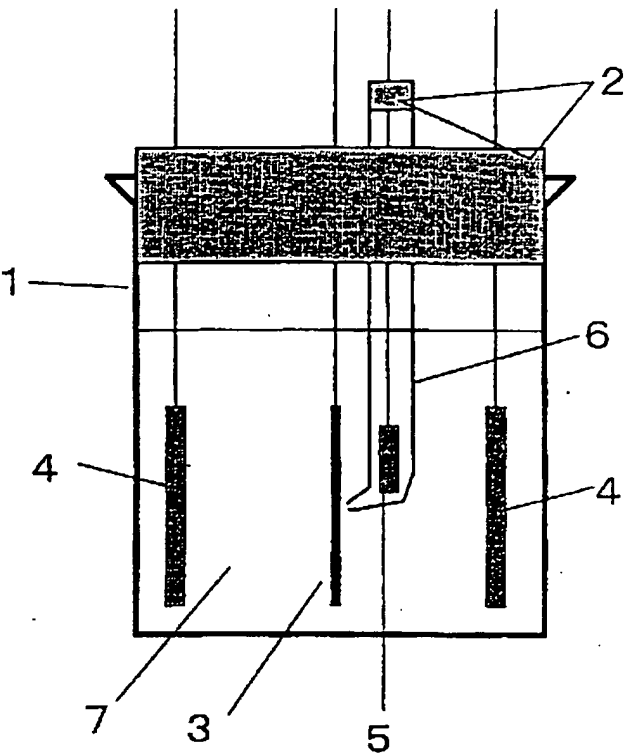
[Claim(s)]

[Claim 1] The manufacture method of the electrode for nonaqueous electrolyte cells characterized by carrying out preferential grinding of the aforementioned graphite using the aforementioned active material in the manufacture method of the electrode for nonaqueous electrolyte cells which applies the electrode active material layer which consists of an active material, graphite which presents the shape of a scale, and a binder on a charge collector after passing the aforementioned graphite through 2 times or more of pulverization processes.

[Claim 2] The manufacture method of the electrode for nonaqueous electrolyte cells according to claim 1 which is larger than the diameter of a centriole of the aforementioned active material.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of the electrode for nonaqueous electrolyte cells which applied the electrode active material layer which consists of an active material, graphite which presents the shape of a scale, and a binder on the charge collector about the manufacture method of the electrode for nonaqueous electrolyte cells.

[0002]

[Description of the Prior Art] Occlusion and the lithium ion rechargeable battery to emit are put in practical use in the lithium in the high discharge potential and the nonaqueous electrolyte cell of high service capacity recently. The electrode of this cell uses an active material as an active material layer paint using a binder, and on a charge collector, it plasters and dries and it is manufactured. Except for a part, electrical conductivity is bad and, as for the active material used for an electrode, for this reason, electric conduction material is used. If the role of electric conduction material is important and there is no electric conduction material in \*\* and others effectively in an electrode, fault, like the capacity of a cell becomes low or a cycle life becomes bad will occur. In a lithium ion rechargeable battery, when carbon is used, for example as an active material by the negative electrode, and a lithium goes into an active material, and it expands and comes out, it contracts. In a lithium ion rechargeable battery, in order to repeat charge and discharge, an active material will repeat expansion contraction. The contact nature of an active material and electric conduction material becomes bad at the time of contraction, and, for this reason, a cell deteriorates gradually. The negative electrode which uses carbon black, such as acetylene black, as electric conduction material, for example, makes "alkali metal an active material as a nonaqueous electrolyte rechargeable battery, nonaqueous electrolyte rechargeable battery to which it has nonaqueous electrolyte and a positive electrode, and the electric conduction material of the aforementioned positive electrode is characterized by the bird clapper from a lot of metal Ti fine particles and a small amount of carbon black Use graphite as LiMn 2O<sub>4</sub> and electric conduction material as " (JP,62-15761,A) and an active material. for example, "-- the nonaqueous electrolyte rechargeable battery which consists of the positive electrode, the negative electrode, and nonaqueous electrolyte which make a subject LiMn 2O<sub>4</sub> and graphite, and is characterized by the rate of the graphite in the total quantity of the above LiMn 2O<sub>4</sub> and graphite being 8 - 22 % of the weight -- There is " (JP,1-105459,A) etc. Moreover, it is the heat treatment object of for example, "phenol system resin as the manufacture method with the related electrode for cells. In the manufacturing method of the electrode for cells which has the poly acene system skeletal structure whose atomic ratios of a hydrogen atom / carbon atom are 0.5-0.05, and consists of the insoluble and infusible nature base whose specific-surface-area value by the BET adsorption method is 600m<sup>2</sup>/g at least manufacturing method of the electrode for cells characterized by applying or pressurization adhering on a base material or it mixes the powder of this insoluble and infusible nature base with electric conduction material and a binder and carries out pressing of this mixture There is " (JP,63-301460,A) etc.

[0003]

[Problem(s) to be Solved by the Invention] There was if the adhesion to the charge collector of a paint film tends to separate bad since the surface area of acetylene black is large, when carbon black, such as acetylene black, is used for aforementioned JP,62-15761,A as electric conduction material of a publication, a problem that a paint film became hard too much, it was bad inflexible, and an electrode became easy to break. For example, although the flexibility of a paint film was good in the case given [ aforementioned ] in JP,1-105459,A, what has the small mean particle diameter of graphite had the bad cycle life, and the large thing was a thing by which the effect as electric conduction material is seldom demonstrated using graphite as electric conduction material, when many amounts were not put in. Moreover, although particle size of electric conduction material is made small in invention of JP,63-301460,A, the cycle life was bad when graphite with a small particle size was used. this invention offers the electrode for nonaqueous electrolyte cells by which charge-and-discharge properties, such as service capacity and a charge-and-discharge cycle life, are good, and the physical characteristic has been improved in view of the above troubles.

[0004]

[Means for Solving the Problem] That the above-mentioned technical problem should be solved, wholeheartedly, after this invention persons performed the trituration process of this graphite twice or more in manufacture of the electrode for nonaqueous electrolyte cells using the graphite which presents the shape of an active substance and a scale as a result of research, by carrying out preferential grinding of this graphite using this active substance, the aforementioned technical problem solved them, they found out that the purpose could be attained, and reached this invention. Namely, this invention is set to the manufacture method of the electrode for nonaqueous electrolyte cells which applies the electrode active material layer which consists of (1) active material, graphite which presents the shape of a scale, and a binder on a charge collector. The manufacture method of the electrode for nonaqueous electrolyte cells characterized by carrying out preferential grinding of the aforementioned graphite using the aforementioned active material after passing the aforementioned graphite through 2 times or more of trituration processes, (2) The manufacture method of the electrode for nonaqueous electrolyte cells the aforementioned (1) publication which is larger than the diameter of a centriole of the aforementioned active substance, (3) The above (1) whose loadings of electric conduction material are 0.1 in paint film - 15wt%, or the manufacture method of the electrode for nonaqueous electrolyte cells given in (2), (4) The manufacture method of the electrode for nonaqueous electrolyte cells the above (1) whose active material is a negative-electrode active material, or given in (2), and (5) active materials are related with the manufacture method of the electrode for nonaqueous electrolyte cells the above (1) which is a positive active material, or given in (2).

[0005]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. this invention is aimed at offering the electrode for nonaqueous electrolyte cells by which charge-and-discharge properties, such as service capacity and a charge-and-discharge cycle life, and the physical characteristic of a paint film have been improved. In the electrode of a nonaqueous electrolyte cell, if some things are removed, since the electrical conductivity of an active material is bad, electric conduction material is used. Although with many amounts of electric conduction material generally tends to pull out the performance which the active material has, when it puts in mostly, the amount of active materials in volume will become less, and capacity will become less as a cell. For this reason, to lessen an electrical conducting material is tried hard, pulling out the performance of an active material. Moreover, although degradation whose capacity decreases takes place whenever a nonaqueous electrolyte rechargeable battery repeats use, it becomes impossible for the contact nature of the active material in an electrode and electric conduction material to become bad one of the causes by which the nonaqueous electrolyte rechargeable battery deteriorates, and to take out the electrical and electric equipment outside, and it is possible to deteriorate as a cell. Usually, although carbon black, graphite, etc., such as acetylene black, are used for electric conduction material and specific surface area of acetylene black is large, if an active material is carbon, it is thought that the contact nature with that is not so good. Moreover, the adhesion to a charge collector tends to separate bad, or an electrode paint film becomes hard, the flexibility of an electrode becomes bad, the paint film using acetylene black is rolled round, and fault, like an electrode sometimes goes out tends to generate it. For this reason, the ratio of area and the surface area of the whole acetylene black in contact with the active material does not have [ that acetylene black tends to take the gestalt which gathered ] the comparatively [ with a large specific surface area ] large front face of acetylene black. If the amount of acetylene black is reduced for the purpose of an improvement of the physical characteristic of an electrode, the effect as electric conduction material will become low.

[0006] If compared with acetylene black, the flexibility of the electrode using graphite is good. Since specific surface area was small compared with acetylene black, in order that graphite might make [ many / as possible ] the contact surface of an active material and graphite, it used what has a small particle size, and was putting in many amounts. the more particle size is small to the publication of the electric conduction material of aforementioned JP,63-301460,A, the more it is indicated by it that it is effective -- as aforementioned, when graphite with a small particle size is used, a cycle life is bad Since particle size is small, this is considered because relation of electric conduction material is bad. Moreover, although the nonaqueous electrolyte rechargeable battery using  $\text{LiMn}_2\text{O}_4$  and graphite is indicated by JP,1-105459,A as aforementioned and the amount of graphite is good eight to 22% of the weight, if many a certain degree generosity is not put in, it means that the effect as electric conduction material is not demonstrated. This will be for the contact surface of electric conduction material and an active material not to increase, if many amounts are not put in, since the specific surface area of electric conduction material is small. Although the electrode with a sufficient cycle life can do the large electric conduction material of particle size comparatively if many amounts are used, since the amount of active materials in the part volume becomes less, the capacity as a cell will become small.

[0007] The graphite which presents the shape of a scale is used for the electric conduction material used in this invention. Such graphite is a natural graphite or an artificial graphite, and the configuration presents the shape of a scale. The shape of a scale in this invention points out the configuration to which the laminating of the thin layers, such as the shape of the shape of the shape of a scale and a scale, a thin film integrated circuit, stratified, and a mica, was



carried out. As graphite which presents the shape of such a scale, there are LF series of a China-Vietnam graphite industrial place, the UFG series of Showa Denko, KS series of LONZA, MICROCARBO-G series of the Kansai thermochemistry, EKOSU carbon series of EKOSU Research Institute, scale-like graphite produced naturally, scale-like graphite, etc. The diameter of a centriole has desirable 1-100 micrometers, and its 4-50 micrometers are more desirable. There is a lithium content metallic oxide expressed with the general formula of  $\text{LiXMyO}_2$  (M is a metal) as an usable positive active material in this invention or same metallic sulfide.  $\text{LiCoO}_2$ ,  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$  grade are desirable. The mean particle diameter has desirable 1-30 micrometers, and its 7-20 micrometers are more desirable. Although there are amorphous carbon, petroleum coke, coal corks, a vapor-growth carbon fiber, a nongraphitizing carbon, a polymer carbon, a stannic-acid ghost, etc. as an usable negative-electrode active material in this invention, in this invention, a nongraphitizing carbon with a high degree of hardness and a polymer carbon are desirable. A polymer carbon points out the carbon material which heat-treats the high polymer which has the structure of cross linkage in an inert atmosphere, and is obtained, and is obtained by carbonization of a cellulose, phenol resin, a furfural resin, poly para-phenylene, a polyacrylonitrile, etc. The diameter of a centriole of a negative-electrode active material has desirable 1-30 micrometers, and its 4-15 micrometers are more desirable. this invention has the feature in the point that an effect is demonstrated in an amount also with little graphite with a large particle size. Particle size does not almost become small even if specific surface area will increase if the cleavage also of the graphite with a large particle size is carried out, since graphite has cleavage nature. However, if graphite tends to unfold the thing which stack-made the stack easy to carry out and shearing force etc. is given poor, it will tend to carry out a stack too many. For example, if a ball mill etc. tends to grind graphite, although trituration will be carried out, a stack is also a plain-gauze cone. Although what carried out the stack is measured as a field with a measurement gas, in respect of contact to an active material, the field is not used effectively. If \*\* is applied to what carried out the stack, a measurement gas will not be abreast measured by fields, either. The diameter of a grain which it is going to grind so that the stack of the trituration of graphite may not be difficultly carried out at such a point will become small.

[0008] In this invention, graphite is ground through 2 times or more of processes. First, graphite is ground by the particle size which he wishes using a jet mill etc. Usually, graphite will choose the thing of the particle size which it gets down and a user considers as hope by which what was ground is marketed. Next, if this is ground so that a cleavage may be carried out using media with a ball mill etc., graphite cannot change most particle size and can make thickness thin. Thus, by passing through 2 times or more of trituration processes, while particle size of graphite has been large, specific surface area increases. However, the stack of them is carried out and umbrella density is large. It can avoid making the particle size as small as possible in this invention, making the effective field which can contact an active material at graphite by carrying out preferential grinding of an active material and the graphite for the graphite which ground and carried out the stack with the ball mill etc. The diameter of a centriole of graphite is larger than the diameter of a centriole of an active material, and a book. Although the loadings of electric conduction material change with specific surface area of an active material etc., they are desirable, and are more desirable. [ 1 - 10wt% of ] [ 0.1 in paint film - 15wt% of ] The diameter of a centriole is measured using laser grading-analysis meters, such as a micro truck by Nikkiso Co., Ltd., and says the diameter of accumulation percent whose frequency accumulation is 50%. Preferential grinding has the dry grinding which used on-GUMIRU of Hosokawa Micron CORP. etc., wet grinding using kneading equipment, etc. In this invention, it says making an active material act carrying out preferential grinding of the graphite using an active material on graphite, and removing the stack of graphite, and/or grinding graphite further. If the stack of the graphite which presents the shape of a scale without breaking an active material not much, since the degree of hardness is comparatively high removes an active material and it is performed still more powerfully by a degree of hardness being low and the graphite which presents the shape of a scale, and the graphite which presents the shape of a scale in the preferential grinding of an active material having lubricity, graphite will be ground more. The following preferential grinding becomes easy about graphite by making it pass through 2 times or more of trituration processes in this way, and electric conduction material is \*\*\*\*\* effectively. Moreover, in a lithium ion rechargeable battery, since \*\*\*\*\* as electric conduction material and \*\*\*\*\* as an active material will be carried out if graphite is used for a negative electrode, it is advantageous also in respect of capacity.

[0009] When performing preferential grinding by dry type, an active material is set up and blended with a high ratio in the possible range to the whole quantity of the electric conduction material which consists of graphite which presents the shape of a scale first, this is supplied to on-GUMIRU or a jet mill, impulse force and shearing force are applied to graphite from an active material, and the stack of graphite is removed, and/or it grinds. If needed, the material which runs short so that it may become the last compounding ratio made contemptuous glance-like is added, and distribution by stirring mixers, such as a hyper-mixer, a dissolver, and a Sand-grinder mill, is performed, and a final adjustment is performed so that the conditions of an application machine may be suited in an electrode active material layer paint. When performing preferential grinding with wet, an active material is set up and blended with a high ratio in the possible range to the whole quantity of the electric conduction material which consists of graphite which presents the

shape of a scale first, this is supplied to a kneading machine, impulse force and shearing force are applied to graphite from an active material, and the stack of graphite is removed, and/or it grinds. In using a kneading machine for preferential grinding, it is necessary to blend the amount of material corresponding to the kneading capacity of the kneading machine to be used, and to fully knead, and if kneading operation is not carried out so that there may be no opening in a kneading machine, trituration of graphite will become inadequate and it will be hard coming to attain the purpose of this invention. Moreover, as a paint is produced with electric conduction material, an active material, binding material, and a solvent as an alternative way and a shear rate becomes large by narrow gap formula dispersers, such as an ultra dace spar, about this, shearing force is applied, the stack of graphite is removed by the active material, and/or it grinds.

[0010] the mixed rate of electric conduction material and an active material -- 0.1 - 40 weight section -- it is 2 - 15 weight section preferably The equipment which gives shearing between the rotation blades and kneading tubs which are called a kneader (kneader) is said, and the form may be independent processing type and consecutive-processing type any, and can mention an open-type kneader, a pressurized type kneader, etc. to the above-mentioned kneading machine as an independent processing type example. Since it is unsuitable that an open type attains the purpose of this invention since the upper part is opened wide and an opening arises and a pressurized type can set an opening as the minimum, it is a book most efficiently. moreover, it is desirable from what-izing can be carried out [ \*\*\*\* ] for including after treatment, such as pretreatment of preliminary mixture etc., kneading, and dilution, the dissolution, without spoiling the effect of this invention, although it will compare with a pressurized type and an opening will arise slightly, since it sends out (feed) and has structure, if a consecutive-processing type kneader is used As an example of the rotation blade used for such a kneader, sigma type, Z type, a cam die, a roller type, S type, a fish-tail type, the Banbury type, etc. can be hung up. As these kneaders' example, independent type kneaders, such as MS formula pressure-type kneader of the Moriyama factory, Continuation kneaders, such as extruders, such as a KRC kneader of a Kurimoto steel place, un-2 powder flannel, Kobe steel, and Toshiba Machine Furthermore, the table-top-type kneader by incorporated company inlet company, the kneader made from the Takabayashi \*\*\*\*, Inc., 2 roll mills, a Banbury mixer, etc. can be raised as equipment of others which have the function which can mention a small thing like the lab plastic strike mill of an incorporated company Oriental energy machine, or a Brabender, and is similar to these kneaders. the polymer which has thermoplastics or rubber elasticity as an usable binder in this invention -- a kind -- or it can mix and use and fluorine system polymer, polyvinyl alcohol, a carboxymethyl cellulose, hydroxypropylcellulose, a regenerated-cellulose diacetyl cellulose, polyvinyl chloride, a polyvinyl pyrrolidone, polyethylene, polypropylene, EPDM, sulfonation EPDM, SBR, a polybutadiene, a polyethylene oxide, etc. can be mentioned as an example of a binder Also in these, it is 1.5 or less [ 0.75 or more ], fluorine-containing \*\* polymer has that desirable whose atomic ratio of a fluorine atom / carbon atom is 1.3 or less [ 0.75 or more ] still more preferably, and when this value is larger than 1.5, the capacity of a cell is not fully obtained, but when it is less than 0.75, a binder dissolves in the electrolytic solution. As such fluorine-containing \*\* polymer, a polytetrafluoroethylene, A polyvinylidene-fluoride and fluoride vinylidene-3 fluoride [ ethylene ] copolymer, An ethylene-tetrafluoroethylene copolymer, a propylene-tetrafluoroethylene copolymer, etc. are mentioned. Furthermore, the fluorine-containing \*\* polymer which replaced the hydrogen of a principal chain by the alkyl group can also be used. What selective-dissolution nature is shown for also in these (the solubility over the electrolytic solution is low and there is a solvent which can dissolve) is desirable. For example, although it is hard to dissolve in the solvent of a carbonate system used for the electrolytic solution in the case of fluoride vinylidene system polymer, it can dissolve in solvents, such as N.N-dimethylformamide and N-methyl pyrrolidone. Although the loadings of such a binder change with the specific surface area of an active material or electric conduction material, grain size, intensity of the electrode made into the purpose, etc., they are desirable, and are more desirable. [ 3 - 15wt% of ] [ 2 in paint film - 20wt% of ]

[0011] moreover, as such a solvent for electrode active material layer paints The general organic solvent can be used. specifically Saturated hydrocarbons, such as a hexane Aromatic hydrocarbons, such as toluene and a xylene, a methanol, ethanol, Alcohols, such as propanol and a butanol, an acetone, a methyl ethyl ketone, Ketones, such as a methyl isobutyl ketone and a diisobutyl ketone, ethyl acetate, Ether, such as ester, such as butyl acetate, a tetrahydrofuran, a dioxane, and diethylether, Although organic solvents, such as halogenated hydrocarbons, such as amides, such as N.N-dimethylformamide, N-methyl pyrrolidone, N, and N-dimethylacetamide, ethylene chloride, and chlorobenzene, can be raised the inside of these -- the solvent of an amide system -- fluorine-containing \*\* polymer -- eye the hatchet which can be dissolved -- it is desirable, and even if these solvents are independent, they can use even two or more sorts of mixed things Furthermore, although aluminum, copper, stainless steel, nickel, titanium, a baked carbon, etc. can be used, for example although it is good anything, if it is the electronic-conduction object which does not cause a chemical change in the constituted cell as a charge collector of such electrode active material composition, and these front faces may be made to process carbon, nickel, titanium, or silver further, if oxidation resistance, the flexibility of an electrode, cost, etc. are especially taken into consideration, an aluminum foil or copper foil is desirable.

On this charge collector, the reverse rolling method, the direct rolling method, the blade method, Although an electrode active material composition paint is applied by the applying methods generally learned well, such as the knife method, the extrusion method, the curtain method, the gravure rolling method, the bar coat method, the dipping method, the kiss coat method, and the squeeze method The extrusion method is desirable especially, and the surface state of a good application layer can be obtained by selecting solvent composition of a paint, and dryness conditions so that it may be applied the speed for 5-100m/. Moreover, as for the thickness of an application layer, it is desirable to adjust by press working of sheet metal generally adopted after the application, the processing pressure is 0.2 - 10 t/cm, and 10-150 degrees C of a working temperature are desirable, although the thickness, length, and width of an application layer are determined by the size of a final cell.

[0012]

[Example]

(Negative electrode) The active material layer was produced as follows (example 1).

(Active material layer paint composition)

Active material Nongraphitizing carbon (4.2 micrometers of diameters of a centriole) : 80 Electric conduction material Product made from LONZA Graphite KS75 10 Binder Elf Atochem Japan KYNAR741 : 10 Polyvinylidene fluoride (PVDF)

Solvent N-methyl-2-pyrrolidone (NMP) : 150 A unit is the weight section PVDF. It is NMP about 10 weight sections. It dissolves in the 150 weight sections and is a binder solution. The 160 weight sections were produced. The jet mill ground electric conduction material, the thing of 18 micrometers of diameters of a centriole was produced, next, the ball mill ground by having made zirconia beads into media for 7 hours, and that whose BET specific surface area is 19m<sup>2</sup>/g was obtained. Active material 80 weight sections and ground electric conduction material Preferential grinding of the 10 weight sections was supplied and carried out to on-GUMIRU for 20 minutes. The above-mentioned binding-material solution was added to this, it mixed by the hyper-mixer, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of an example 1 was obtained.

[0013] (Example 2) The jet mill ground the electric conduction material of an example 1, the diameter of a centriole produced 12 micrometers, next, the pulverization time in a ball mill was 20m<sup>2</sup>/g, and also the BET specific surface area carried out like the example 1 in 5 hours. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of an example 2 was obtained.

[0014] (Example 3) The jet mill ground the electric conduction material of an example 1, the diameter of a centriole produced 8 micrometers, next, the pulverization time in a ball mill was 21m<sup>2</sup>/g, and also the BET specific surface area carried out like the example 1 in 4 hours. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of an example 3 was obtained.

[0015] (Example 4) It changed into the scale-like natural graphite (18 micrometers of diameters of an LF-18made from China-Vietnam graphite A centriole) which had the electric conduction material of an example 1 ground, and the pulverization time in a ball mill was 20m<sup>2</sup>/g, and also the BET specific surface area performed this like the example 1 in 9 hours. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of an example 4 was obtained.

[0016] (Example 5) The jet mill ground the electric conduction material of an example 1, the diameter of a centriole produced 3.5 micrometers, next, in 30 minutes, the pulverization time in a ball mill was 20m<sup>2</sup>/g, and also the BET specific surface area carried out like the example 1. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of an example 5 was obtained.

[0017] (Example 1 of comparison) Electric conduction material of an example 1 It changes into acetylene black (DENKI KAGAKU KOGYO DIN a turnip rack), and is an active material. 80 weight sections and acetylene black Preferential grinding of the 10 weight sections was supplied and carried out to on-GUMIRU for 20 minutes. The binding-material solution was added to this, it mixed by the hyper-mixer, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the

roller-press machine, it cut in the predetermined size, and the electrode of the example 1 of comparison was obtained. [0018] (Example 2 of comparison) Electric conduction material of an example 1 It changes into a vapor-growth carbon fiber (Showa Denko VGCF), and is an active material. 80 weight sections and vapor-growth carbon fiber Preferential grinding of the 10 weight sections was supplied and carried out to on-GUMIRU for 20 minutes. The binding-material solution was added to this, it mixed by the hyper-mixer, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of the example 2 of comparison was obtained.

[0019] (Example 3 of comparison) The jet mill ground the electric conduction material of an example 1, the thing of 18 micrometers of diameters of a centriole was produced, next, the ball mill ground by having made zirconia beads into media for 7 hours, and that whose BET specific surface area is  $19\text{m}^2/\text{g}$  was obtained. Active material 80 weight sections and electric conduction material 10 weight sections are supplied and blended dryly with a hyper-mixer, and it is a binder solution to this mixture. The 160 weight sections were added, stirring mixture was carried out for 60 minutes, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of the example 3 of comparison was obtained.

[0020] (Example 4 of comparison) The jet mill ground the electric conduction material of an example 1, and the thing of 18 micrometers of diameters of a centriole was produced. Active material 80 weight sections and electric conduction material 10 weight sections are blended dryly by the hyper-mixer, and it is a binder solution to this mixture. The 160 weight sections were added, stirring mixture was carried out for 60 minutes, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of the example 4 of comparison was obtained.

[0021] (Example 5 of comparison) The jet mill ground the electric conduction material of an example 1, and the thing of 18 micrometers of diameters of a centriole was produced. Active material 80 weight sections and ground electric conduction material Preferential grinding of the 10 weight sections was supplied and carried out to on-GUMIRU for 20 minutes. The binding-material solution was added to this, it mixed by the hyper-mixer, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of rolling copper foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of the example 5 of comparison was obtained.

[0022] The sample to the evaluation method (electrode characteristic) examples 1-5 and the examples 1-5 of comparison was cut to 25mm long and 20mm wide, the electrode layer was removed for the upper-limit section by width of face of 5mm, and it left the electrode layer of 20mm angle. Spot welding of the stainless steel line was carried out to the upper-limit section which removed the electrode layer as a lead, and this electrode (operation pole) was created. As shown in drawing 1, the cell for charge-and-discharge volumetry was produced, and charge and discharge were performed as follows. One pair of counter electrodes 4 using the lithium board connected to the stainless steel line into the beaker 1, Luggin capillary 6 which has the same reference pole 5, and the electrode (operation pole) 3 further created above in the middle of a counter electrode are arranged. to the electrolytic solution 7 the 1 mol [l.] lithium perchlorate was confined in the beaker and the Luggin capillary with the silicon plug using what was dissolved in the mixed solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate as an electrolyte salt, it came out, and the cell for measurement was created And it carried out by having repeated charge and discharge 5 times in the ranges from 0V to 2V (PotentialvsLi/Li+) by the 2mA constant current in this cell, the capacity at the time of 1st Li ion emission was measured, and it considered as initial capacity. Moreover, the 5th capacity was also measured and it considered as the charge-and-discharge cycle property.

[0023] (Positive electrode) The active material layer was produced as follows (example 6).

(Active material layer paint composition)

Active material  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  : 93 ~~10 micrometers of diameters of a centriole~~ Electric conduction material Product made from LONZA Graphite KS75 : 4 Binder Elf ARUKEMU Japan KYNAR741 : 3 Polyvinylidene fluoride (PVDF) Solvent N-methyl-2-pyrrolidone (NMP) : 67 A unit is the weight section PVDF. It is NMP about 3 weight sections. It dissolves in 67 weight sections and is a binder solution. 70 weight sections were produced. The jet mill ground electric conduction material, the thing of 18 micrometers of diameters of a centriole was produced, next, the ball mill ground by having made zirconia beads into media for 7 hours, and that whose BET specific surface area is  $19\text{m}^2/\text{g}$  was obtained. Active material Preferential grinding of 93 weight sections and the ground electric conduction material 4 weight section was supplied and carried out to on-GUMIRU for 20 minutes. The above-mentioned binding-material solution 70

weight section was added to this, stirring mixture was carried out for 60 minutes by the hyper-mixer, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of an aluminum foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of an example 6 was obtained.

[0024] (Example 7) The jet mill ground the electric conduction material of an example 6, the diameter of a centriole produced 3.5 micrometers, next, in 30 minutes, the trituration time in a ball mill was 20m<sup>2</sup>/g, and also the BET specific surface area carried out like the example 6. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of an aluminum foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of an example 7 was obtained.

[0025] (Example 6 of comparison) The electric conduction material of an example 6 is changed into acetylene black (DENKI KAGAKU KOGYO DIN a turnip rack), and it is an active material 93. The weight section and electric conduction material Preferential grinding of the 4 weight sections was supplied and carried out to on-GUMIRU for 20 minutes. The binding-material solution was added to this, it mixed by the hyper-mixer, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of an aluminum foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of the example 6 of comparison was obtained.

[0026] (Example 7 of comparison) The jet mill ground the electric conduction material of an example 6, the thing of 18 micrometers of diameters of a centriole was produced, next, the ball mill ground by having made zirconia beads into media for 7 hours, and that whose BET specific surface area is 19m<sup>2</sup>/g was obtained. Active material 93 weight sections and electric conduction material 4 weight sections are blended dryly by the hyper-mixer, and it is a binder solution to this mixture. 70 weight sections were added, stirring mixture was carried out for 60 minutes, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of an aluminum foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of the example 7 of comparison was obtained.

[0027] (Example 8 of comparison) The jet mill ground the electric conduction material of an example 6, and the thing of 18 micrometers of diameters of a centriole was obtained. Active material 93 weight sections and electric conduction material 4 weight sections are blended dryly by the hyper-mixer, and it is the above-mentioned binder solution to this mixture. 70 weight sections were added, stirring mixture was carried out for 60 minutes, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of an aluminum foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of the example 8 of comparison was obtained.

[0028] (Example 9 of comparison) The jet mill ground the electric conduction material of an example 6, and the thing of 18 micrometers of diameters of a centriole was produced. Active material 93 weight sections and ground electric conduction material Preferential grinding of the 4 weight sections was supplied and carried out to on-GUMIRU for 20 minutes. The binding-material solution was added to this, it mixed by the hyper-mixer, and the active material layer paint was obtained. After applying and drying the paint same at the rear face after applying and drying the done paint in a blade coating machine at charge collector one side of an aluminum foil, compression molding was carried out with the roller-press machine, it cut in the predetermined size, and the electrode of the example 9 of comparison was obtained.

[0029] The evaluation method JIS (adhesion) K 5400 8.5.1 It examined according to the squares method and the adhesion to the aluminum foil of a paint film was investigated. One side of the paint film applied to both sides of an aluminum foil was scratched, the cut was attached in a grid pattern using the tester (11 ERICHSEN MODEL 295 1mm interval edge), and mark were given according to JIS.

(Electrode characteristic) In the sample of examples 6 and 7 and the examples 6-9 of comparison, production of the cell for evaluation was performed like the negative electrode. And it carried out by having repeated charge and discharge 5 times in the ranges from 3V to 4.2V (PotentialvsLi/Li+) by the 6mA constant current in this cell, the capacity at the time of 1st Li ion occlusion was measured, and it considered as initial capacity. Moreover, the 5th capacity was also measured and it considered as the charge-and-discharge cycle property.

[0030]

[Table 1]

	ボールミル 粉 碎	混合粉碎	導 電 材	初期容量 (mAh/g)	5 t h 容量 (mAh/g)
実施例 1	有 り	有 り	グラファイト	3 9 4	3 6 5
実施例 2	有 り	有 り	グラファイト	3 8 7	3 4 2
実施例 3	有 り	有 り	グラファイト	4 0 1	3 7 5
実施例 4	有 り	有 り	グラファイト	3 9 6	3 6 6
実施例 5	有 り	有 り	グラファイト	3 6 8	2 7 0
比較例 1	有 り	有 り	アセチレンブラック	3 5 2	1 9 8
比較例 2	有 り	有 り	V G C F	3 6 4	2 2 0
比較例 3	有 り	無 し	グラファイト	3 8 1	1 9 8
比較例 4	無 し	無 し	グラファイト	3 7 2	2 0 2
比較例 5	無 し	有 り	グラファイト	3 7 7	2 5 8

[0031]

[Table 2]

	ボールミル 粉 碎	混合粉碎	導 電 材	初期容量 (mAh/g)	5 t h 容量 (mAh/g)	付 着 性 基盤目試験
実施例 6	有 り	有 り	グラファイト	1 9 5	1 9 0	8 点
実施例 7	有 り	有 り	グラファイト	1 9 9	1 5 2	8 点
比較例 6	有 り	有 り	アセチレンブラック	1 8 4	1 7 9	2 点
比較例 7	有 り	無 し	グラファイト	1 8 8	1 1 8	8 点
比較例 8	無 し	無 し	グラファイト	1 6 5	9 6	8 点
比較例 9	無 し	有 り	グラファイト	1 8 3	1 4 1	8 点

[0032]

[Effect of the Invention] As shown in Table 1, a few quantity of graphite is also pulling out and carrying out the property of \*\*\*\*\* by carrying out preferential grinding of the graphite through 2 times or more of pulverization processes. The capacity of the created cell also becomes large and the cycle property which suggests the life of a rechargeable battery is also improving. It turns out that the cycle property of little graphite is improving graphite by performing preferential grinding through [ from Table 2 ] 2 times or more of pulverization processes. Moreover, the electrode of adhesion using graphite is good and has obtained the high score also in the cross cut adhesion test.

[Translation done.]